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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Burcau

(43) International Publication Date
27 March 2003 (27.03.2003)

PCT

(10) International Publication Number
WO 03/024227 A2

(51) International Patent Classification[7]: A01N 47/36
// (A01N 47/36, 47:36, 43:88, 37:40)

(21) International Application Number: PCT/EP02/10541

(22) International Filing Date:
19 September 2002 (19.09.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1733/01 20 September 2001 (20.09.2001) CH

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/024227 A2

(54) Title: HERBICIDAL COMPOSITION

(57) Abstract: A herbicidal composition which, in addition to comprising customary inert formulation adjuvants, comprises as active ingredient a mixture of at least two compounds selected from the group amidosulfuron, bentazone, bifenox, diflufenican, dicamba, dimethenamid, fenoxaprop-P-ethyl, flurtamone, glufosinate, iodosulfuron-methyl (sodium), bromoxynil, ioxynil, beflubutamid, imazosulfuron, pyraflufen (-ethyl), cinidon-ethyl, 2,4 D, MCPA, MCPP, picolinafen, pendimethalin, imazethapyr, imazapic, imazapyr, imazaquin, imazamox, imazamethabenz-methyl and mesosulfuron, with a mixture of picolinafen and cinidon-ethyl being excluded.

Herbicidal composition

The present invention relates to a novel herbicidal synergistic composition comprising a herbicidal active ingredient combination that is suitable for the selective control of weeds in crops of useful plants, for example in cereal crops.

The invention relates also to a method of controlling weeds in crops of useful plants and to the use of the novel composition for that purpose.

The compounds amidosulfuron, bentazone, bifenox, diflufenican, dicamba, dimethenamid, flurtamone, glufosinate, fenoxaprop-P-ethyl, iodosulfuron-methyl (sodium), bromoxynil, ioxynil, beflubutamid, imazosulfuron, cinidon-ethyl, 2,4 D, MCPA, MCPP, picolinafen, pendimethalin, pyraflufen (-ethyl) and imazethapyr exhibit herbicidal activity, as described, for example, in The Pesticide Manual, 12th Edition (BCPC), 2000. Mesosulfuron is known from EP-A-559 814 and WO 01/24633, in which the herbicidal activity of this compound is described.

Surprisingly, it has now been found that a combination of variable amounts of at least two active ingredients from the above list exhibits a synergistic action that is capable of controlling, both pre-emergence and post-emergence, the majority of weeds occurring especially in crops of useful plants without causing any appreciable damage to the useful plant.

There is therefore proposed in accordance with the present invention a novel synergistic composition for selective weed control which, in addition to comprising customary inert formulation adjuvants, comprises as active ingredient a mixture of at least two compounds selected from the group amidosulfuron, bentazone, bifenox, diflufenican, dicamba, dimethenamid, fenoxaprop-P-ethyl, flurtamone, glufosinate, iodosulfuron-methyl (sodium), bromoxynil, ioxynil, beflubutamid, imazosulfuron, pyraflufen (-ethyl), cinidon-ethyl, 2,4 D, MCPA, MCPP, picolinafen, pendimethalin, imazethapyr, imazapic, imazapyr, imazaquin, imazamox, imazamethabenz-methyl and mesosulfuron, with a mixture of picolinafen and cinidon-ethyl being excluded.

It is extremely surprising that combinations of those active ingredients exceed the additive action on the weeds to be controlled that is to be expected in principle and thus broaden the range of action of the two active ingredients especially in two respects: firstly, the rates of application of the individual compounds are reduced while a good level of action is maintained and, secondly, the composition according to the invention achieves a high level of weed control also in those cases where the individual substances, in the range of low rates of application, have become useless from the agronomic standpoint. The result is a considerable broadening of the spectrum of weeds and an additional increase in selectivity in respect of the crops of useful plants, as is necessary and desirable in the event of an unintentional overdose of active ingredient. The composition according to the invention, while retaining excellent control of weeds in useful plants, also allows greater flexibility in succeeding crops.

The composition according to the invention can be used against a large number of agronomically important weeds, such as Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Bromus, Apera, Alopecurus, Matricaria, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola and Veronica. The composition according to the invention is suitable for all methods of application conventionally used in agriculture, e.g. pre-emergence application, post-emergence application and seed dressing. The composition according to the invention is suitable especially for controlling weeds in crops of useful plants such as cereals and maize and more especially for controlling weeds in cereals. "Crops of useful plants" are to be understood as including those which have been made tolerant to herbicides or classes of herbicides as a result of conventional methods of breeding or genetic engineering.

The composition according to the invention comprises the said active ingredients in any mixing ratio, but usually has an excess of one component over the other. Preferred mixing ratios of the active ingredients are from 100:1 to 1:100 and from 50:1 to 1:50.

The following combinations have proved to be especially effective compositions: amidosulfuron + dicamba, bentazone + dicamba, flurtamone + dimethenamid, fenoxaprop-P-ethyl + bromoxynil, fenoxaprop-P-ethyl + ioxynil, glufosinate + dimethenamid, iodosulfuron-methyl (sodium) + dicamba, iodosulfuron-methyl (sodium) + bentazone, iodosulfuron-methyl (sodium) + mesosulfuron, ioxynil + dicamba, ioxynil + bentazone, and ioxynil + mesosulfuron. The mixtures comprising iodosulfuron-methyl (sodium) or mesosulfuron are especially preferred.

The rate of application may vary within wide limits and depends on the nature of the soil, the method of application (pre- or post-emergence; seed dressing; application to the seed furrow; no tillage application etc.), the crop plant, the weed to be controlled, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. The active ingredient mixture according to the invention can generally be applied at a rate of from 0.001 to 1.5 kg of active ingredient mixture per ha.

The mixtures according to the invention may be employed in unmodified form, that is to say as obtained in synthesis. Preferably, however, they are formulated in customary manner, together with the adjuvants conventionally used in formulation technology, such as solvents, solid carriers or surfactants, for example into emulsifiable concentrates, directly sprayable or dilutable solutions, wettable powders, soluble powders, dusts, granules or microcapsules, as described in WO 97/34483, pages 9 to 13. As with the nature of the compositions, the methods of application, such as spraying, atomising, dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The formulations, i.e. the media, preparations or compositions comprising the mixtures according to the invention and also, as appropriate, one or more solid or liquid formulation adjuvants, are prepared in a manner known *per se*, e.g. by intimately mixing and/or grinding the active ingredients with the formulation adjuvants, e.g. solvents or solid carriers. In addition, surface-active compounds (surfactants) may also be used in the preparation of the formulations.

Examples of solvents and solid carriers are given, for example, in WO 97/34485, page 6. Depending on the nature of the active ingredients to be formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties. Examples of suitable anionic, non-ionic and cationic surfactants are listed, for example, in WO 97/34485, pages 7 and 8. Also suitable for the preparation of the herbicidal compositions according to the invention are the surfactants conventionally employed in formulation technology, which are described, *inter alia*, in "McCutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81.

The herbicidal formulations usually contain from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of active ingredient mixture, from 1 to 99.9 % by weight of a solid or liquid formulation adjuvant, and from 0 to 25 % by weight, especially from 0.1 to 25 % by weight, of a surfactant.

Whereas commercial products are usually formulated as concentrates, the end user will normally employ dilute formulations. The compositions may also comprise further ingredients, such as stabilisers, e.g. vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, e.g. silicone oil, preservatives, viscosity regulators, binders, tackifiers and also fertilisers or other active ingredients. Preferred formulations have especially the following compositions:
(% = percent by weight)

Emulsifiable concentrates:	
active ingredient mixture:	1 to 90 %, preferably 5 to 20 %
surfactant:	1 to 30 %, preferably 10 to 20 %
liquid carrier:	5 to 94 %, preferably 70 to 85 %
Dusts:	
active ingredient mixture:	0.1 to 10 %, preferably 0.1 to 5 %
solid carrier:	99.9 to 90 %, preferably 99.9 to 99 %
Suspension concentrates:	
active ingredient mixture:	5 to 75 %, preferably 10 to 50 %
water:	94 to 24 %, preferably 88 to 30 %
surfactant:	1 to 40 %, preferably 2 to 30 %
Wettable powders:	
active ingredient mixture:	0.5 to 90 %, preferably 1 to 80 %
surfactant:	0.5 to 20 %, preferably 1 to 15 %
solid carrier:	5 to 95 %, preferably 15 to 90 %
Granules:	
active ingredient mixture:	0.1 to 30 %, preferably 0.1 to 15 %
solid carrier:	99.5 to 70 %, preferably 97 to 85 %

The following Examples illustrate the invention further, but do not limit the invention.

F1. Emulsifiable concentrates	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	25 %	50 %
calcium dodecylbenzenesulfonate	6 %	8 %	6 %	8 %
castor oil polyglycol ether (36 mol of ethylene oxide)	4 %	-	4 %	4 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	4 %	-	2 %
cyclohexanone	-	-	10 %	20 %
arom. hydrocarbon mixture C_9-C_{12}	85 %	78 %	55 %	16 %

Emulsions of any desired concentration can be obtained from such concentrates by dilution with water.

F2. Solutions	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	50 %	90 %
1-methoxy-3-(3-methoxy-propoxy)-propane	-	20 %	20 %	-
polyethylene glycol MW 400	20 %	10 %	-	-
N-methyl-2-pyrrolidone	-	-	30 %	10 %
arom. hydrocarbon mixture C_9-C_{12}	75 %	60 %	-	-

The solutions are suitable for use in the form of microdrops.

F3. Wettable powders	a)	b)	c)	d)
active ingredient mixture	5 %	25 %	50 %	80 %
sodium lignosulfonate	4 %	-	3 %	-
sodium lauryl sulfate	2 %	3 %	-	4 %
sodium diisobutylnaphthalene-sulfonate	-	6 %	5 %	6 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	1 %	2 %	-
highly dispersed silicic acid	1 %	3 %	5 %	10 %
kaolin	88 %	62 %	35 %	-

The active ingredient is mixed thoroughly with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of any desired concentration.

F4. Coated granules	a)	b)	c)
active ingredient mixture	0.1 %	5 %	15 %
highly dispersed silicic acid	0.9 %	2 %	2 %
inorganic carrier (diameter 0.1 - 1 mm) e.g. $CaCO_3$ or SiO_2	99.0 %	93 %	83 %

The active ingredient is dissolved in methylene chloride and applied to the carrier by spraying, and the solvent is then evaporated off *in vacuo*.

F5. Coated granules	a)	b)	c)
active ingredient mixture	0.1 %	5 %	15 %
polyethylene glycol MW 200	1.0 %	2 %	3 %
highly dispersed silicic acid	0.9 %	1 %	2 %
inorganic carrier (diameter 0.1 - 1 mm) e.g. $CaCO_3$ or SiO_2	98.0 %	92 %	80 %

The finely ground active ingredient is uniformly applied, in a mixer, to the carrier moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

F6. Extruder granules	a)	b)	c)	d)
active ingredient mixture	0.1 %	3 %	5 %	15 %
sodium lignosulfonate	1.5 %	2 %	3 %	4 %
carboxymethylcellulose	1.4 %	2 %	2 %	2 %
kaolin	97.0 %	93 %	90 %	79 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

F7. Dusts	a)	b)	c)
active ingredient mixture	0.1 %	1 %	5 %
talcum	39.9 %	49 %	35 %
kaolin	60.0 %	50 %	60 %

Ready-to-use dusts are obtained by mixing the active ingredient with the carriers and grinding the mixture in a suitable mill.

F8. Suspension concentrates	a)	b)	c)	d)
active ingredient mixture	3 %	10 %	25 %	50 %
ethylene glycol	5 %	5 %	5 %	5 %
nonylphenol polyglycol ether	-	1 %	2 %	-

(15 mol of ethylene oxide)				
sodium lignosulfonate	3 %	3 %	4 %	5 %
carboxymethylcellulose	1 %	1 %	1 %	1 %
37 % aqueous formaldehyde solution	0.2 %	0.2 %	0.2 %	0.2 %
silicone oil emulsion	0.8 %	0.8 %	0.8 %	0.8 %
water	87 %	79 %	62 %	38 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

It is often more practical for the active ingredients of the mixtures according to the invention to be formulated separately and to be brought together in the desired mixing ratio in the applicator in the form of a "tank mixture" in water shortly before application.

Biological Examples:

Example B1: Pre-emergence test:

The test plants are sown in pots under greenhouse conditions. A standard soil is used as cultivation substrate. At a pre-emergence stage the herbicides are applied to the surface of the soil both alone and in admixture. The rates of application are governed by the optimum concentrations determined under field or greenhouse conditions. The tests are evaluated 2 to 4 weeks later (100% action = plant has completely died; 0% action = no phytotoxic action). The mixtures used in this test exhibit good results.

Example B2: Post-emergence test:

The test plants are raised to a post-application stage in pots under greenhouse conditions. A standard soil is used as cultivation substrate. At a post-emergence stage the herbicides are applied to the test plants both alone and in admixture. The rates of application are governed by the optimum concentrations determined under field or greenhouse conditions. The tests are evaluated 2 to 4 weeks later (100% action = plant has completely died; 0% action = no phytotoxic action). The mixtures used in this test exhibit good results.

What is claimed is:

1. A herbicidal synergistic composition which, in addition to comprising customary inert formulation adjuvants, comprises as active ingredient a mixture of at least two compounds selected from the group amidosulfuron, bentazone, bifenox, diflufenican, dicamba, dimethenamid, fenoxaprop-P-ethyl, flurtamone, glufosinate, iodosulfuron-methyl (sodium), bromoxynil, ioxynil, beflubutamid, imazosulfuron, pyraflufen (-ethyl), cinidon-ethyl, 2,4 D, MCPA, MCPP, picolinafen, pendimethalin, imazethapyr, imazapic, imazapyr, imazaquin, imazamox, imazamethabenz-methyl and mesosulfuron, with a mixture of picolinafen and cinidon-ethyl being excluded.

2. A method of controlling undesired plant growth in crops of useful plants, which comprises allowing a herbicidally effective amount of a composition according to claim 1 to act on the crop plant or the locus thereof.

3. A method according to claim 2, wherein the crop plant is a cereal.